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THE CONDENSATION AND EVAPORATION OF GAS MOLECULES

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Several years ago,[1] I gave evidence that atoms of tungsten, molybdenum, or platinum vapors, striking a clean, dry glass surface in high vacuum, are condensed as solids at the first collision with the surface. Subsequently, similar evidence[2] was obtained in connection with a study of chemical reactions in gases at low pressures. It was concluded that in general, when gas molecules strike a surface, the majority of them "do not rebound from the surface by elastic collisions, but are held by cohesive forces until they evaporate from the surface." In this way a theory of adsorption was developed[3] which has been thoroughly confirmed by later experiments. It was stated: "The amount of material adsorbed depends on a kinetic equilibrium between the rate of condensation and the rate of evaporation from the surface. Practically every molecule striking the surface condenses (independently of the temperature). The rate of evaporation depends on the temperature (van't Hoff's equation) and is proportional to the *fraction* of the surface covered by the adsorbed material."

R. W. Wood[4] described some remarkable experiments in which a stream of mercury atoms impinges upon a plate of glass held at a definite temperature. With the plate cooled by liquid air, all the mercury atoms condense on the plate, but at room temperature all the atoms appear to be diffusely reflected.

The whole question of the evaporation, condensation, and possible reflection of gas molecules has been discussed at some length in two recent papers[5,6]. It was pointed out that, in Wood's experiments, there are excellent reasons for believing that the mercury vapor actually condenses on the glass at room temperature, but evaporates so rapidly that no visible deposit of mercury is formed. Further evidence of the absence of reflection is furnished by the operation of the 'Condensation Pump.'[7]

In a second paper, Wood[8] gives an account of some still more striking experiments. A stream of cadmium atoms, striking the walls of a well exhausted glass bulb, does not form a visible deposit unless the glass is at a temperature below about −90°C. If, by cooling the bulb for a moment with liquid air, a deposit is started, this continues to grow in thickness even after it is warmed to room temperature. From these and similar observations, Wood concludes that:

1. Cadmium atoms all condense on cadmium surfaces at any temperature.
2. Cadmium atoms condense on glass only if it is at a temperature below about −90°C. At higher temperatures, nearly all the atoms are reflected.

This viewpoint leads to no explanation of the changes in the reflection coefficient. The results of Wood's experiments may, however, be explained by the theory that all the atoms, striking either the glass or the cadmium surface, condense, and that subsequent evaporation accounts for the apparent reflection.

Cadmium atoms on a glass surface are acted on by totally different forces from those holding cadmium atoms on a cadmium surface. When a thick deposit of cadmium which has been distilled onto glass in vacuum, is heated quickly above its melting-point, the molten cadmium gathers together into little drops on the surface of the glass. In other words, molten cadmium does not wet glass. Therefore cadmium atoms have a greater attractive force for each other than they have for glass. Thus, single cadmium atoms on a glass surface evaporate off at a lower temperature than that at which they evaporate from a cadmium surface. It is not unreasonable to assume that in Wood's experiments, even at −90°C., the cadmium evaporated off of the glass as fast as it condensed upon it.

This theory possesses the advantage that it automatically explains the apparent reflection of cadmium atoms from a glass surface at room temperature, and indicates why this effect should be absent at low temperatures.

We shall see, moreover, that this condensation-evaporation theory explains many other facts incompatible with the reflection theory.

Let us examine for a moment the essential differences between these two theories. Wood describes his remarkable experimental results, but he has not attempted to discuss the mechanism of the underlying processes. It is clear that Wood uses the term 'reflection' merely to express the fact that under certain conditions no visible deposit is formed when the atoms strike a surface. From this point of view, condensation followed by evaporation is the same as reflection. In considering the possible mechanisms of the process, however, we must sharply distinguish between the two theories.

When an atom strikes a surface and rebounds elastically from it, we are justified in speaking of this process as a reflection. Even if the collision is only partially elastic, we may still use this term. The idea that should be expressed in the word 'reflection' is that the atom leaves the surface by a process which is the direct result of the collision of the atom against the surface.

On the other hand, according to the condensation-evaporation theory, there is no direct connection between the condensation and subsequent evaporation. The chance that a given atom on a surface will evaporate in a given time is not dependent on the length of time that has elapsed since the condensation of that atom. Atoms striking a surface have a certain average 'life' on the surface, depending on the temperature of the surface and the intensity of the forces holding the atom. According to the 'reflection' theory, the life of an atom on the surface is simply the duration of a collision, a time practically independent of temperature and of the magnitude of the surface forces.

To determine definitely which of the two theories corresponds best with the facts, I have repeated Wood's experiments under somewhat modified conditions. A small spherical bulb, together with an appendix containing cocoanut charcoal, was heated to 600°C. for about four hours while being exhausted by a condensation pump. A liquid-air trap was placed between the pump and the bulb. Some cadmium was purified by distillation and was distilled into the bulb, which was then sealed off from the pump. The cadmium in the bulb was then all distilled into the lower hemisphere. By heating this lower half of the bulb to about 140°C., the upper half remained clear, but by applying a wad of cotton, wet with liquid air, to a portion of the upper hemisphere, a uniform deposit formed within less than a minute and continued to grow, even after the liquid air was removed.

When the liquid air was applied only long enough to start a deposit, it was found in the first experiments that the deposit did not grow uniformly, but became mottled, or showed concentric rings. The outer edges of the deposit were usually much darker than the central portions. By cooling the cocoanut charcoal in liquid air, this effect disappeared entirely and the cadmium deposits became remarkably uniform in density. It is thus evident that traces of residual gas may prevent the growth of the deposit, particularly in those places which have been the most effectively cooled. This is probably due to the adsorption of the gas by the cooled metal deposit. This gas is apparently retained by the metal, even after it has warmed up to room temperature, so that vapor condensing on the surface evaporates off again at room temperature.

These results indicate how enormously sensitive such metal films are to the presence of gas. However, by using liquid air and charcoal continually during the experiments, most of these complicating factors were eliminated.

If all the cadmium is distilled to the lower half of the bulb and this is then heated to 220° in an oil bath while the upper half is at room temperature, a fog-like deposit is formed on the upper part of the bulb in about fifteen seconds. This deposit is very different from that obtained by cooling the bulb in liquid air. Microscopic examination shows that it consists of myriads of small crystals. According to the condensation-evaporation theory, the formation of this fog is readily understood. Each atom of cadmium, striking the glass at room temperature, remains on the surface for a certain length of time before evaporating off. If the pressure is very low, the chance is small that another atom will be deposited, adjacent to the first, before this has had time to evaporate. But at higher pressures this frequently happens. Now if two atoms are placed side by side on a surface of glass, a larger amount of work must be done to evaporate one of these atoms than if the atoms were not in contact. Not only does the attractive force between the cadmium atom and the glass have to be overcome, but also that between the two cadmium atoms. Therefore the rate of evaporation of atoms from pairs will be much less than that of single atoms. Groups of three and four atoms will be still more stable. Groups of two, three, four, etc., atoms will thus serve as nuclei on which crystals can grow. The tendency to form groups of two atoms increases with the square of the pressure, while groups of three form at a rate proportional to the cube of the pressure. Therefore the tendency for a foggy deposit to be formed increases rapidly as the pressure is raised or the temperature of the condensing surface is lowered.

On the other hand, according to the reflection theory, there seems to be no satisfactory way of explaining why the foggy deposit should form under these conditions.

Experiments show clearly that when a beam of cadmium vapor at very low pressure strikes a given glass surface at room temperature, no foggy deposit is formed, although when the *same quantity* of cadmium is made to impinge against the surface in a shorter time (and therefore at higher pressure) a foggy deposit results. This fact constitutes strong proof of the condensation-evaporation theory.

A deposit of cadmium of extraordinary small thickness will serve as a nucleus for the condensation of more cadmium at room temperature. Let all the cadmium be distilled to the lower half of the bulb. Now heat the lower half to 60°C. Apply a wad of cotton, wet with liquid air, to a portion of the upper half for one minute, and then allow the bulb to warm up to room temperature. Now heat the lower half of the bulb to 170°C. In about thirty seconds a deposit of cadmium appears which rapidly grows to a silver-like mirror. This deposit only occurs where the bulb was previously cooled by liquid air.

The question arises: how much cadmium could have condensed on the bulb in one minute while the lower part of the bulb was at 60°C.?

The vapor pressure of cadmium has been determined by Barus[9] between the temperatures 549° and 770°C. If the logarithms of the pressures are plotted against the reciprocals of the temperature, a straight line is obtained from which the following equation for the vapor pressure (in bars) is obtained as a function of absolute temperature

$$\log p = 11.77 - \frac{6060}{T} \qquad (1)$$

At 60°C. the vapor pressure of cadmium is of the order of magnitude of 4×10^{-7} bars. Now the number of molecules of gas which strike a square centimeter of surface per second is

$$n = 2.65 \times 10^{19}\, p/\sqrt{M\,T} \qquad (2)$$

Substituting $M = 112$, $T = 333°$, and $p = 4 \times 10^{-7}$, we find that with saturated cadmium vapor at 60°C., $n = 5 \times 10^{10}$ atoms per second per square centimeter.

The maximum number of atoms of cadmium which can condense in *one minute* on a spot cooled in liquid air when the lower part of the bulb is at 60°C. is therefore 3.0×10^{12} atoms per square centimeter. The diameter of a cadmium atom is approximately 3.1×10^{-8} cm., so that it would require 1.0×10^{15} atoms to cover 1 square centimeter with a single layer of atoms.

Therefore the deposit which forms in one minute with the vapor from cadmium at 60°, contains only enough cadmium atoms to cover 3/1000 of the surface of the glass. Yet this deposit serves as an effective nucleus for the formation of a visible deposit.

If the lower part of the bulb is heated to 78° instead of 60°, the nucleus formed by applying liquid air for one minute causes a visible deposit to grow more rapidly (with the lower part of the bulb at 170°). But the nucleus obtained with temperatures above about 78° are not any more effective than those formed at 78°.

A calculation similar to that above shows that the deposit formed in one minute at 78° contains 2.5×10^{13} atoms per square centimeter, or enough to cover 25/1000 of the surface. If we consider that the surface of the glass contains elementary spaces each capable of holding one cadmium atom, the chance that any given cadmium atom will be adjacent to another is $1-(1-0.025)^7$, or 0.16. When the surface is allowed to warm up, the single atoms evaporate, but the pairs remain. The surface is then covered to the extent of 16% of 25/1000, or 4/1000. About 2% of the atoms striking such a surface will fall in positions adjacent to those atoms already on the surface. With cadmium vapor at 170°, 1.4×10^{15} atoms per square centimeter strike the surface each second, so that 2.8×10^{13} would condense in the first second around the 4×10^{12} atoms remaining on the surface. Thus in only a few seconds the whole surface becomes covered with a layer of cadmium atoms. This explains why a surface only partially covered with cadmium atoms can serve so effectively as a nucleus. If a much smaller fraction than 0.025 of the surface is covered, however, there is a long delay in completing the first layer of atoms, so that the visible deposit is formed much more slowly.

The above experiments prove that the range of atomic forces is very small and that they act only between atoms practically in contact with each other. Thus a surface covered by a single layer of cadmium atoms behaves, as far as condensation and evaporation are concerned, like a surface of massive cadmium. This absence of transition layer is in accord with my theory of heterogeneous reactions.[10]

One of the best proofs of the correctness of the condensation-evaporation theory was obtained in experiments in which nuclei formed at liquid air temperature, were not allowed to warm up to room temperature, but only to −40°C. In this case the nuclei were formed in one minute from cadmium vapor at 54°C. The nuclei which were kept at −40°C. developed rapidly into cadmium mirrors in cadmium vapor at 170°, while those at room temperature developed extremely slowly. A still more striking demonstration of the theory was obtained when one of the nuclei was allowed to warm up to room temperature and then cooled to −40° before exposure to cadmium vapor at 170°. This nucleus did not develop nearly as rapidly as that which had not been allowed to warm up to room temperature.

These experiments prove that single cadmium atoms actually evaporate off of a glass surface at temperatures below room temperature, although they do not do so at an appreciable rate from a cadmium surface.

This theory affords a very satisfactory explanation of Moser's breath figures on glass and the peculiar effects observed in the formation of frost crystals on window panes. In fact, the theory appears capable of extension to the whole subject of nucleus formation, including, for example, the crystallization of supercooled liquids.

The final paper will be submitted to the *Physical Review* for publication.

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THE NINTH SATELLITE OF JUPITER

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Communicated by G. E. Hale, January 18, 1917

The Ninth Satellite of Jupiter, whose discovery was announced in these PROCEEDINGS, **1**, 1915, (12), was rediscovered at the Lick Observatory during the 1915 opposition and the observations secured then were forwarded to me before publication. On the basis of these positions the preliminary orbit,[1] derived from observations in 1914 at the time of discovery, was approximately corrected so that the satellite could be more easily located at the 1916 opposition. Four images of it have been found on plates taken here by Mr. Shapley with the 60-inch reflector. Although the computed position was in error by about 2′ there can be no doubt as to the identification of the object.

Observations are now available for three oppositions and the orbit is being corrected to satisfy them. Although the final elements will differ considerably from those now available, our present knowledge of